Interaction of nitrogen with vacancy defects in N^+-implanted ZnO studied using a slow positron beam

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ZnO crystals were implanted with N^+, O^+, and Al^+, and co-implanted with O^+/N^+ and Al^+/N^+ ions. Positron annihilation measurements indicate introduction of vacancy clusters upon implantation. In the N^+-implanted and Al^+/N^+ co-implanted samples, these vacancy clusters are only partially annealed at 800 °C, as compared with their entire recovery in the O^+- and Al^+-implanted samples at 800–900 °C, suggesting a strong interaction between nitrogen and vacancy clusters. However, in the O^+/N^+ co-implanted sample, most vacancy clusters disappear at 800 °C. Probably oxygen scavenges nitrogen to enhance the annealing of the vacancy clusters. Upon further annealing at 1000–1100 °C, nitrogen also forms stable complexes with thermally generated vacancies. These nitrogen-related vacancy complexes need high-temperature annealing at 1200–1250 °C to be fully removed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2037847]

ZnO as a wide-band-gap semiconductor has potential application in short-wavelength optoelectronic devices.[1] However, some fundamental problems still remain unsolved in this material, which have hindered its device application. One critical problem is the *p*-type doping control. Although a few attempts have produced *p*-type ZnO by doping with nitrogen[2–4] or codoping with N+Ga (see Ref. 5) and N+Al,[6] high-quality and reproducible *p*-type doping is still a challenge. Ion implantation is an important method for the incorporation of dopants in the selected area of semiconductors at controllable amounts. Therefore, N^+ implantation is likely to be a promising method for obtaining *p*-type ZnO layers. However, implantation introduces large amounts of defects, which may compensate or deactivate the nitrogen acceptors by forming defect complexes.[7] Hence, it is of great importance to investigate the recovery process of implantation-induced defects, and the probable interactions between nitrogen and various defects.

In this work, we incorporated nitrogen into ZnO by N^+ implantation as well as O^+/N^+ and Al^+/N^+ co-implantation. Positron annihilation spectroscopy is well suited for studying vacancy defects in semiconductors.[8] Some recent works have reported identification of vacancy defects in both as-grown and irradiated ZnO.[9–12] Implantation-induced defects and their recovery were, therefore, studied using a slow positron beam.

Samples were hydrothermal-grown *n*-type ZnO single crystals (SPC Goodwill). Ion implantation was conducted at room temperature using a 400 keV implanter. A box-shaped implantation layer with thickness of 500–600 nm was formed by performing multiple implantation using seven different ion energies ranging from 50 to 380 keV. The total implantation dose for each ion was approximately 4×10^{15} cm^{-2}. For the O^+/N^+ and Al^+/N^+ co-implantation, the dose ratios of $O^+:N^+$ and $Al^+:N^+$ were 1:1 and 0.5:1, respectively. The implanted samples were annealed in nitrogen ambient for 30 min at 200–1250 °C. The Doppler broadening of annihilation radiation was measured using a slow positron beam (E=0.2–30 keV). The *S* parameter was used to characterize the measured spectra, which is the ratio of the central region (511±0.77 keV) to the total area of the annihilation peak (511±8.5 keV). A pulsed slow positron beam was used to measure the positron lifetime. Hall measurements were performed using the van der Pauw method to characterize the electrical properties of the implanted samples.

Figure 1 shows the *S* parameter as a function of the incident positron energy (*S*-*E* curve) for the samples before and after ion implantation. In the unimplanted sample, positron lifetime measurement shows only a bulk lifetime of about 182 ps,[11] indicating that the concentration of vacancy defects is under the detection limit. After ion implantation, the *S* parameters show a large increase as compared with the

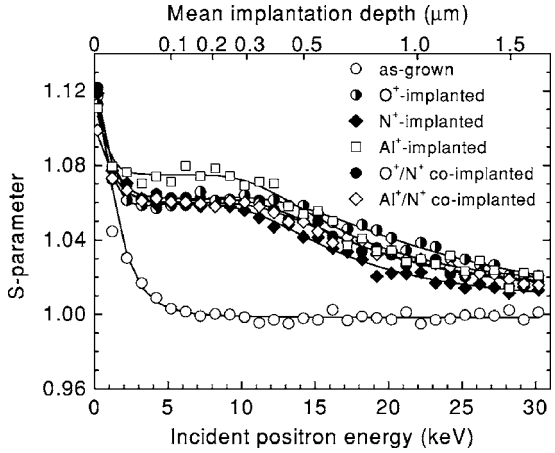

FIG. 1. *S*-*E* curves measured for the ZnO samples before and after ion implantation.

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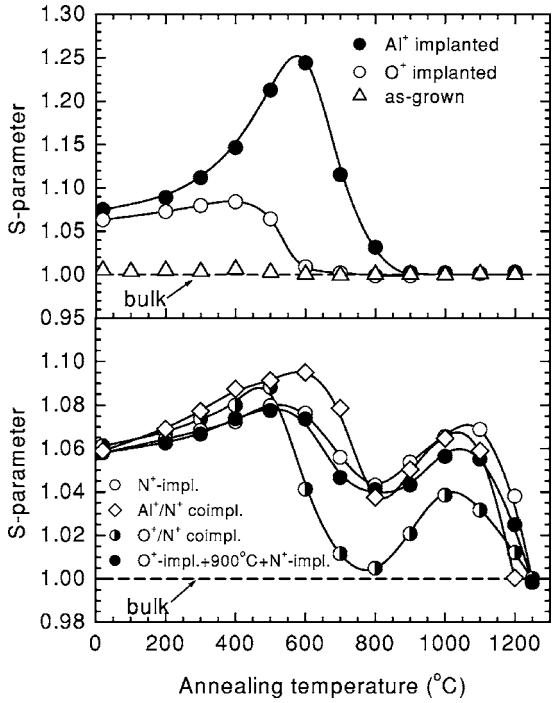

FIG. 2. Average *S* parameter in the implanted region ($E=5-9$ keV) as a function of annealing temperature for the as-grown and ion-implanted ZnO.

unimplanted sample, indicating the introduction of vacancy defects. There is a plateau region in the energy range of 3–11 keV, which corresponds to the box-shaped implantation layer. The *S* parameters increase to about 1.06 for most of the implanted samples, except that in the Al^+-implanted one, it is a little higher, that is, 1.08. This suggests that the defects are mainly vacancy clusters.[8]

Figure 2 shows the average *S* parameters at $E=5-9$ keV as a function of annealing temperature for all the implanted samples. For the O^+-implanted sample, there are two annealing processes. The *S* parameter first increases up to 1.08 at 400 °C, then it decreases, and reaches the bulk value at 800 °C. This annealing behavior can be explained by the agglomeration of the vacancies into a larger size and subsequent recovery of these vacancies. The Al^+-implanted sample shows a similar annealing behavior. However, the *S* parameter increases to a high value of 1.25 after annealing at 600 °C, indicating formation of microvoids as reported previously.[13] Further annealing up to 900 °C causes full recovery of all the detectable vacancies.

In the case of the N^+-implanted sample, however, the annealing behavior of vacancy defects is significantly different from that just described. That is, there are four annealing processes. The first two processes (0–500 °C and 500–800 °C) are similar to that of the O^+-implanted sample. It is interesting to note that, even after annealing at 800 °C, the *S* parameter remains rather high value. Furthermore, after annealing in the third process (800–1100 °C), the *S* parameter increases again. The full recovery of the *S* parameter takes place at 1100–1250 °C. Similar annealing behavior is also observed for the Al^+/N^+ co-implanted ZnO, as shown in Fig. 2.

The high *S* parameters at annealing temperature of 800 °C in the N^+-implanted and Al^+/N^+ co-implanted samples imply that large amounts of vacancy clusters still remain. Clearly this is due to nitrogen impurities. Without nitrogen, the vacancies can be easily removed, such as the cases in the O^+- or Al^+-implanted samples. It is therefore suggested that the vacancy clusters are probably stabilized by nitrogen impurities through the formation of complexes, which results in the imperfect annealing at 800 °C, as shown earlier.

We believe that the abnormal increase of the *S* parameter after annealing at above 800 °C is also related to nitrogen, as we do not observe such peculiar behavior in the as-grown or Al^+-implanted ZnO up to 1200 °C [Fig. 2(a)]. In the O^+-implanted sample, the *S* parameter also remains unchanged up to 900 °C, in contrast to the increase in the N^+-implanted one. No such abnormal annealing behavior was observed in other ion-implanted ZnO samples either.[14] Most probably nitrogen-related defect complexes are created after annealing at above 800 °C. At such high temperatures, thermal vacancies are expected to be generated. These thermal vacancies may trap nitrogen to form stable vacancy–nitrogen complexes, and survive after cooling down. Further annealing at 1200–1250 °C probably leads to the dissociation of the vacancy–nitrogen complexes, or the evaporation of nitrogen, and hence, the recovery of vacancies. Such vacancy complexes may also be generated in the as-grown nitrogen-doped ZnO. Uedono *et al.*[10] observed a significant increase of the *S* parameter after annealing the nitrogen doped ZnO film at 850 °C, while in the undoped ZnO, annealing caused negligible change of the *S* parameter. Garces *et al.*[15] found that after heating the nitrogen-doped ZnO above 800 °C, nitrogen acceptors are transformed into an electrically inactive state. They ascribed this to either the formation of defect complexes or the outdiffusion of nitrogen. Our positron annihilation measurements, thus, demonstrate that nitrogen is possibly deactivated through defect complex formation. The thermally generated vacancy-impurity complexes has also been observed in other semiconductors; for example, the As- and P-doped Si.[16]

For the O^+/N^+ co-implanted sample as well, there are four annealing processes. However, after annealing at 800 °C, the *S* parameter reaches almost the bulk value, suggesting that most vacancy clusters are removed. This is different from the situation of N^+ implantation but similar to that of the O^+ implantation. It suggests that the nitrogen-related vacancy complexes can be effectively removed, or the interaction between nitrogen and vacancy clusters is weakened by co-implantation with oxygen. However, after further annealing above 800 °C, these nitrogen impurities again combine with thermal vacancies. Therefore, the *S* parameter increases.

These explanations are further confirmed by our positron lifetime measurements. As shown in Fig. 3, for the N^+-implanted sample, after annealing at 1100 °C, two lifetime components with $\tau_1=233$ ps and $\tau_2=369$ ps are observed. It is evident that τ_2 corresponds to the vacancy clusters that are stabilized by nitrogen, while τ_1 coincides with the positron lifetime for zinc vacancy (V_{Zn}),[12] and therefore can be attributed to the positron annihilation at the thermally generated V_{Zn}–N pairs. As for the O^+/N^+ co-implanted sample, since the vacancy clusters have been annealed out at 800 °C, only the thermally generated V_{Zn}–N pairs exist after further annealing at 1000 °C, therefore, we observe a single lifetime of approximately 240 ps.

One more indication of the nitrogen–vacancy interaction is the *S*-*W* correlation. For the O^+/N^+ co-implanted sample,

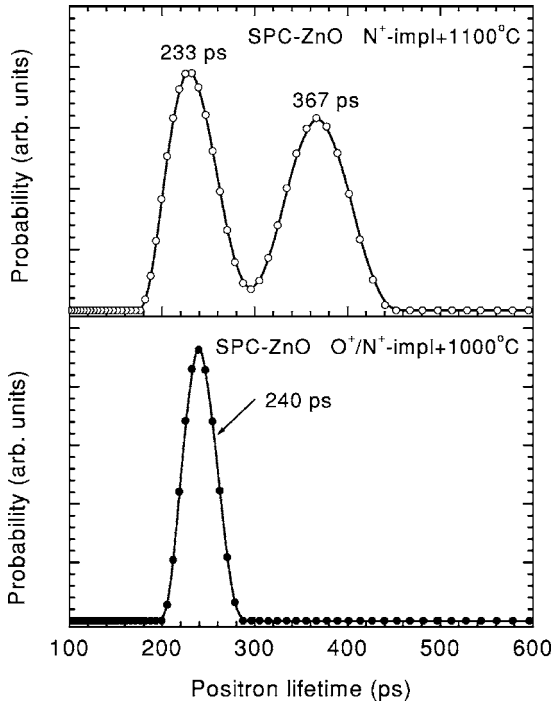

FIG. 3. Positron lifetime in the N^+-implanted and O^+/N^+ co-implanted ZnO after annealing at 1100 and 1000 °C, respectively. The incident positron energy is 7 keV.

deviation of the *S-W* plot from that of the O^+-implanted one can be seen after annealing above 800 °C, indicating V_{Zn}–N complex formation. For the N^+-implanted sample, the *S-W* plot is even more complicated. This is due to the interaction of nitrogen with both vacancy clusters and zinc vacancies.

We also examined another O^+/N^+ co-implanted sample. The O^+-implanted sample after annealing at 900 °C was subsequently implanted with N^+. The annealing behavior for this sample was nearly the same as that of the N^+-implanted one (Fig. 2). This means that only the mobile oxygen can effectively remove the vacancy clusters in the N^+-implanted ZnO. After annealing of the O^+-implanted sample, oxygen atoms occupy the sublattice sites and become immobile. Thus, the annealing behavior of this co-implanted sample is identical to that of the one implanted with nitrogen only.

Hall measurements listed in Table I reveal that after N^+ implantation and final annealing, the implanted layer exhibits *n*-type conductivity, with a sheet resistance in very close proximity to that of the unimplanted sample annealed at 1200 °C. This implies that nitrogen has little contribution to the conductivity. The Al^+/N^+ co-implanted layer also shows *n*-type conductivity. Contrarily, after O^+/N^+ co-implantation and annealing at 800 °C, the implanted layer exhibits a high sheet resistance, 10^7 Ω/□, which is much higher than that of the unimplanted sample annealed at 900 °C. The

TABLE I. Sheet resistance R_S, carrier mobility μ, and conduction type for the as-grown and implanted ZnO samples obtained from Hall measurements.

Sample	$R_S(\omega/\square)$	$\mu(\mathrm{cm^2\,V^{-1}\,s^{-1}})$	Type
As-grown	3.3×10^5	66	*n*
As-grown+900 °C	5×10^3	70	*n*
As-grown+1200 °C	17.7	51	*n*
N^+ impl+1250 °C	11.9	84	*n*
O^+ impl+800 °C	5×10^6	···	SI[a]
Al^+ impl+900 °C	8.6	167	*n*
O^+/N^+ impl+800 °C	10^7	···	SI[a]
Al^+/N^+ impl+1200 °C	9.4	49	*n*

[a]SI: semi-insulating.

O^+-implanted layer also shows rather high resistance after annealing. It is thus inferred that the semi-insulating layer is mostly due to the incorporation of oxygen, which suppresses or compensates donor-type defects.

In summary, nitrogen dopants implanted into ZnO delay the recovery process of the vacancy clusters by forming vacancy complexes. However, by co-implantation of nitrogen with oxygen, vacancy clusters can be effectively annealed at 800 °C. At high temperatures, nitrogen also combines with thermally generated vacancies to form stable complexes. A high temperature of 1200–1250 °C is needed to remove all these nitrogen-related defect complexes.

[1]Y. Chen, D. Bagnall, and T. Yao, Mater. Sci. Eng., B **75**, 190 (2000).
[2]X.-L. Guo, H. Tabata and T. Kawai, J. Cryst. Growth **223**, 135 (2001).
[3]D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
[4]X. Li, Y. Yan, T. A. Gessert, C. L. Perkins, D. Young, C. DeHart, M. Young, and T. J. Coutts, J. Vac. Sci. Technol. A **21**, 1342 (2003).
[5]M. Joseph, H. Tabata, and T. Kawai, Jpn. J. Appl. Phys., Part 2 **38**, L1205 (1999).
[6]J. G. Lu, Z. Z. Ye, F. Zhuge, Y. J. Zeng, B. H. Zhao, and L. P. Zhu, Appl. Phys. Lett. **85**, 3134 (2004).
[7]Eun-Cheol Lee, Y.-S. Kim, Y.-G. Jin, and K. J. Chang, Phys. Rev. B **64**, 085120 (2001).
[8]R. Krause-Rehberg and H. S. Leipner, *Positron Annihilation in Semiconductors, Defect Studies*, Springer Series in Solid-State Sciences Vol. 127 (Springer, Berlin, 1999).
[9]S. Brunner, W. Puff, A. G. Balogh, and P. Mascher, Mater. Sci. Forum **363–365**, 141 (2001).
[10]A. Uedono, T. Koida, A. Tsukazaki, M. Kawasaki, Z. Q. Chen, SF. Chichibu, and H. Koinuma, J. Appl. Phys. **93**, 2481 (2003).
[11]Z. Q. Chen, S. Yamamoto, M. Maekawa, A. Kawasuso, X. L. Yuan, and T. Sekiguchi, J. Appl. Phys. **94**, 4807 (2003).
[12]F. Tuomisto, V. Ranki, K. Saarinen, and D. C. Look, Phys. Rev. Lett. **91**, 205502 (2003).
[13]Z. Q. Chen, M. Maekawa, S. Yamamoto, A. Kawasuso, X. L. Yuan, T. Sekiguchi, R. Suzuki, and T. Ohdaira, Phys. Rev. B **69**, 035210 (2004).
[14]Z. Q. Chen, A. Kawasuso, Y. Xu, H. Naramoto, X. L. Yuan, T. Sekiguchi, R. Suzuki, and T. Ohdaira, J. Appl. Phys. **97**, 013528 (2005).
[15]N. Y. Garces, L. J. Wang, N. C. Giles, L. E. Halliburton, G. Cantwell, and D. B. Eason, J. Appl. Phys. **94**, 519 (2003).
[16]V. Ranki and K. Saarinen, Phys. Rev. Lett. **93**, 255502 (2004).